A Passive Sampler for the Determination of Carbonyl Compounds in Indoor Air Employing *O*-(4-cyano-2-ethoxybenzyl)hydroxylamine as Reactive Adsorbent

Masayuki Onishi,[a] Yoshika Sekine,*,[a] Koichi Sugihara,[b] Kazuya Kitasaka,[b] and Hatsumi Shimajiri[b]

[a]*Department of Chemistry, School of Science, Tokai University, 1117 Kitakaname, Hiratsuka, Kanagawa, 259–1292 Japan and* [b]*Osaka Laboratory, Sumika Chemical Analysis Service, Ltd., 3–1–135, Kasugade-naka, Konohana, Osaka, 554–0022 Japan*

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Authors have developed a new analytical method for gaseous carbonyl compounds in indoor air using a passive sampler. The sampler consists of a porous polyethylene cylinder uniformly packed with *O*-(4-cyano-2-ethoxybenzyl)hydroxylamine (CNET) coated silica gel as a reactive adsorbent. After sampling, CNET derivatives were eluted by acetonitrile and subsequently determined by HPLC. Sampling rates for formaldehyde, acetaldehyde and acetone were determined by a small chamber experiment with a constant gas generation system and resulted in 74 ml/min for formaldehyde, 44 ml/min for acetaldehyde and 42 ml/min for acetone. Effects of exposure time (8 and 24 hr), temperature (10, 25 and 40°C) and relative humidity (31–94%) on the rate were not apparent under the given conditions. The passive sampler was then applied for field measurements of carbonyl compounds in indoor air and gave similar results when compared to active samplings using 2,4-dinitrophenylhydrazine (DNPH) coated cartridges. The Ames test showed the CNET is preferable in safety handling because of its lower mutagenic activities than those of DNPH. Carbonyl compounds can be determined with reduced interference of ozone, because the CNET was less degradable when exposed to ozone compared with DNPH. Therefore, the CNET is a possible alternative to DNPH as trapping reagent in the passive sampling device for the determination of formaldehyde, acetaldehyde and acetone in indoor air.

Key words —— carbonyl compounds, passive sampler, *O*-(4-cyano-2-ethoxybenzyl)hydroxylamine, sampling rate, indoor air

INTRODUCTION

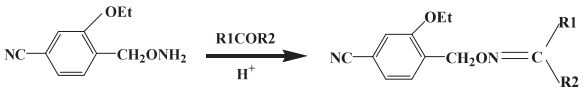
Exposure to carbonyl compounds in indoor air has been known to cause adverse health effects on human health, particularly in relation to idiopathic environmental intolerance, also known as multiple chemical sensitivities.[1,2] Therefore, information of the indoor air concentration levels of carbonyl compounds such as formaldehyde, acetaldehyde and acetone is important for the determination of indoor air quality of occupational and living environments.

Passive samplers, which employ diffusion process based on Fick's law and hence do not require power supply or other services, has been recognized efficient alternative to active sampling for monitoring personal exposure and indoor air concentrations of such indoor air pollutants.[3] In accordance with the Housing Quality Assurance Law, Japan, the passive samplers for formaldehyde and Volatile Organic Compounds (VOCs) are practically used for indoor air quality monitoring to ensure housing performance of newly built houses.

Solid sorbents coated with 2,4-dinitrophenylhydrazine (DNPH) have been used for the determination of carbonyl compounds in active[4–6] and passive sampling methods.[7–12] The reaction between aldehydes/ketones and DNPH is rapid and quantitative in the presence of acid, and the product can be determined by UV-HPLC with excellent sensitivity. However, several problems were pointed out in the use of DNPH, including unstable property of some

*To whom correspondence should be addressed: Department of Chemistry, School of Science, Tokai University, 1117 Kitakaname, Hiratsuka, Kanagawa, 259–1292 Japan. Tel.: +81-463-58-1211; Fax: +81-463-50-2094; E-mail: sekine@keyaki.cc.u-tokai.ac.jp

DNPH derivatives such as acrolein and crotonaldehyde during storage,[13] hazardous property such as mutagenicity[14] and interference of ozone.[15, 16] Recently, *O*-(4-cyano-2-ethoxybenzyl)hydroxylamine (CNET) has been developed as a new trapping reagent of carbonyl compounds in air. The CNET reacts with aldehydes/ketones and gives stable products as follows.



(1)

Akiyama and Nakayama[17] have applied the CNET coated silica gel to active samplings of carbonyl compounds in automobile exhausts and showed following advantages using the CNET. Lower blank levels of carbonyl compounds in the CNET cartridge than those of DNPH cartridge, Stability of CNET derivatives after sampling, especially in acrolein and Successful application to determination of low concentrations of automobile exhaust carbonyl compounds.

Then, we have developed a passive sampler employing the CNET coated silica gel as a reactive sorbent. Using passive sampler, sampling rate, S is a dominant factor for analytical liability. The sampling rate shows a magnitude of diffusive uptake rate of analyte in the passive sampling process and has dimensions of volume per unit time. As shown in Eq.(2), collected amount of carbonyl compounds on adsorbent, W could be converted to air concentration, C using exposure time, t and S, if the adsorbent reduces the concentration of the given analyte at the end of diffusion layer ideally to zero due to sorption or chemical reaction.[3]

$$C = \frac{W}{St} \tag{2}$$

The sampling rate could be estimated from a diffusion coefficient, D of the given analyte and the geometry of the diffusion layer of the passive sampler; $S = DA/L$, A is cross sectional area of diffusion path and L is diffusion path length. However, the sampling rate should be practically determined in advance, because it often depends on the property of adsorbent used[18, 19] and it is difficult to know A/L in practice when using a porous material or membrane as a diffuser.

In this study, CNET was investigated as a potential alternative to DNPH as trapping reagent in the passive sampling device by comparing mutagenic activities and influence of ozone on the stability of the reagents, and evaluating sampling performance of the new passive sampler for the determination of formaldehyde, acetaldehyde and acetone in air.

MATERIALS AND METHODS

Passive Sampler (CNET-P) —— Figure 1 shows a schematic view of the passive sampler, CNET-P. The sampler simply consists of porous polyethylene (PE) cylinder, end caps and CNET coated silica gel inside the PE cylinder. The porous cylinder made of sintered PE particles works as a diffusion filter, which is chemically inert to the carbonyl compounds. The sorbent was prepared as follows. To a suspension of 200 mg of silica gel (Kanto Chemical, Tokyo, Japan, 60N, spherical, 63–210 μm) in 200 ml of acetonitrile, CNET (Sumika Chemical Analysis Service, Osaka, Japan, 476 mg) dissolved in 20 ml of acetonitrile was dropped and stirred for 10 min at room temperature. Subsequently, 200 ml of 85% phosphoric acid/acetonitrile solution was added to the suspension. After stirring for 1 hr at room temperature, the surpernatant was removed by filtration. The residue was thoroughly washed by acetonitrile

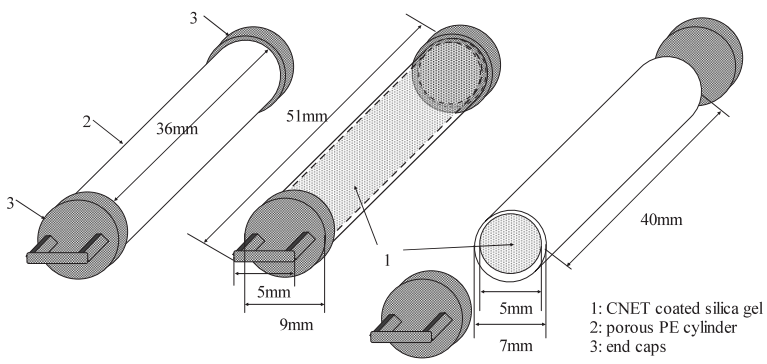


Fig. 1. Schematic View of the Passive Sampler, CNET-P

and dried to give the sorbent. This sorbent is commonly used for active sampler.[17] Amount of coated CNET is 1.0–1.1 mg per 0.3 g of silica gel in a single passive sampler.

Reverse Mutation Assays (Ames Test) —— Mutagenic effects of the CNET and related chemicals were tested by the short-term screening method developed by Ames *et al.*[20,21] The test substance was incubated with special genotype variants of the *Salmonella typhimurium* (*S. typhimurium*; TA98, TA100, TA1535, TA1537) and *Escherichia coli* (*E. coli*; WP2*uvr*A). Four strains of *S. typhimurium* (TA98, TA100, TA1535, TA1537) were used with a known mutational pattern in histidine-operone, so their growth depend on exogenic histidine and are not able to grow on histidine free agar plates. Growth of *E. coli* strain (WP2*uvr*A) depends on exogenic tryptophan as well. By contact with a mutagenic test substance, mutations of the genes can be reverted, so that the bacteria grow again as revertants on the histidine-free or tryptophan-free agar independently of the exogenic amino acid supply and can be counted in colony formation. Test materials were CNET phosphate, reaction product of CNET and formaldehyde (CNET-formaldehyde), DNPH (reagent grade) and DNPH-formaldehyde dissolved in dimethylsulfoxide (DMSO). The Ames test was conducted by Environment Health Science Laboratory, Sumitomo Chemical Co., Ltd. (Osaka, Japan), following a standard operating procedure. Briefly, a mixture of 0.1 ml of the dilution series of test solutions (0–5000 μg/plate), 0.1 ml of bacteria suspension and 0.5 ml of phosphate buffer or S9mix were preincubated for 20 min at 37°C under constant shaking, and subsequently added with top agar and plated. The plate was incubated for 48 hr at 37°C. Then, the colonies were counted and compared with solvent and positive controls. Duplicate plates were examined at each dose of test substances.

Small Chamber Experiment —— The sampling performance of the CNET-P for formaldehyde, acetaldehyde and acetone were investigated using a small chamber (32 l) with a constant gas generation system under controlled temperature (Fig. 2). Diffusion samplers were hanged at the centre of the chamber inside. Mixture of the trace gases was constantly introduced from a gas generator at a flow rate of 2 l/min. Diluted aqueous solutions of reagent grade formaldehyde solution (Kanto Chemical, 40%), acetaldehyde (Kanto Chemical, > 99.9%) and acetone (Kanto Chemical, > 99.9%)

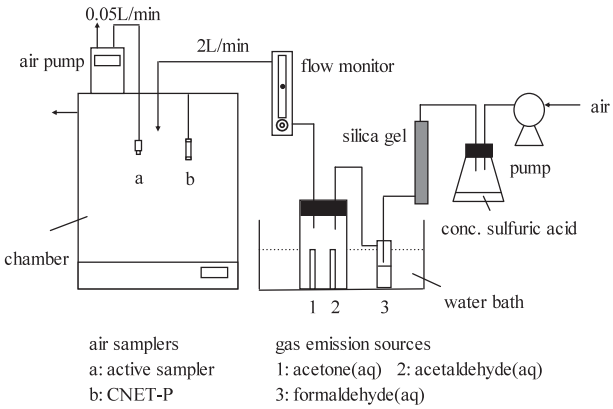


Fig. 2. Layout of the Small Chamber Experiments

in diffusion tubes (Gastec) set in a water bath (25°C) were used for gas emission sources of the generator. A fan thoroughly mixed the air in the chamber. Air concentrations in the chamber were 0.047–0.33 mg/m^3 for formaldehyde, 0.020–1.3 mg/m^3 for acetaldehyde and 0.018–0.41 mg/m^3 for acetone. The exposure time was set at 8 hr, typical sampling time in workplace and 24 hr for monitoring the daily mean indoor air concentration in residence. As a reference to passive sampler, active sampling was simultaneously carried out by pumping air through DNPH coated solid cartridge (Waters, Milford, MA, USA, Xposure short-body) connected with air pump (Sibata Science, Tokyo, Japan, MP-30) at a flow rate of 0.05 l/min for 8 hr (24 l) and 24 hr (72 l). The collection efficiency of the cartridge was examined by passing 72 l of air containing 0.02–1.5 mg/m^3 of formaldehyde, acetaldehyde and acetone through the two cartridges in series. Under these conditions, all of the carbonyl compounds were trapped in the first cartridge and no compounds were found in the second cartridge.

Field Experiment —— To validate the sampling rate determined by small chamber experiments, field tests were conducted at two sites: a room of apartment house with residents and a teaching room of Tokai University from July to September, 2004 and August, 2006. In the field, active samplers were placed alongside as a reference method. Two pairs of a single passive sampler and a pumped DNPH cartridge (0.05 l/min) were deployed together in the rooms for 8 and 24 hr. Numbers of run were 9 in teaching room and 4 in apartment house for each sampling duration.

Effect of Face Velocity on the Sampling Performance —— The effect of air velocity on the sampling performance was investigated by moving the

passive samplers in indoor air, referring the method by Uchiyama *et al.*[11] Ten passive samplers were fixed at intervals of 16 cm of 1.6 m rod in perpendicular to the rod. Then, the samplers were rotated by an electric motor at 45 rpm for 8 hr. A sampler, which was fixed 0.8 m from the central pivot of the rod, corresponded to a face velocity of 4 m/s, measured by an anemometer (Testo, Yokohama, Japan, 405-V1). A pair of the samplers was separately deployed without rotating (static). After rotating, collection amounts of carbonyl compounds in the laboratory air were determined by HPLC.

Influence of Ozone —— Artifact problems may arise when using passive samplers in atmospheres containing relatively high ozone levels. The potential influence of ozone on the CNET was firstly investigated. To 0.01 mg/ml of CNET or DNPH/acetonitrile solution, 0.8 ppm of ozone, generated by ozonizer (Logy Electric, Tokyo, Japan) under purified air (Nippon Sanso, Tokyo, Japan, G2 grade), was bubbled for 5 min at a rate of 1.0 l/min. Similarly, to 0.01 mg/ml of CNET or DNPH/acetonitrile solution, 100 μl of 40% formaldehyde solution (Kanto Chemical) was dropped to form formaldehyde derivatives, and then 0.8 ppm of ozone was bubbled for 5 min at a rate of 1.0 l/min. Afterwards, the solutions were injected to HPLC system. Losses of CNET, DNPH, CNET-formaldehyde and DNPH-formaldehyde were determined from decrease in peak area of corresponding compounds in HPLC chromatogram.

The CNET-P was then exposed to mixed vapours of formaldehyde, acetaldehyde and acetone in the small chamber, as described above, with and without ozone for 8 hr. The ozone concentration in the chamber was set at 0.1 and 0.8 ppm by ozonizer. Simultaneously, DNPH-based passive sampler, DSD-DNPH (Sigma-Aldrich Japan, Tokyo, Japan) was also exposed to the mixture of gases as reference. Collection amounts of carbonyls were determined by HPLC and compared between the two kinds of samplers.

Analytical Procedure —— After sampling, the solid sorbent of the passive sampler was placed in a vial. CNET derivatives were eluted by adding 5 ml of acetonitrile with mild shaking, stand for 30 min and subsequently determined by HPLC. The HPLC system consists of Hitachi (Tokyo, Japan) L-2100 pump, Hitachi L-2400 UV detector and Hitachi D-2500 data processor. The following conditions were used: column, 4.6×250 mm, 5 μm, SUMIPAX ODS D-211 (Sumika Chemical Analysis Service); eluent, 55/45 acetonitrile/deionized water at 1.0 ml/min (isocratic); detection wavelength, 240 nm; injection volume, 20 μl. Dilution series of each CNET derivative (commercially available from Sumika Chemical Analysis Service) were used as analytical standards. Duplicate injections were made for standards, samples and blanks. Samples collected by both active and passive DNPH samplers were determined by HPLC, following the method described by Sekine *et al.*[12]

RESULTS AND DISCUSSION

Mutagenicity

The test substance is considered to be mutagenic when the number of counted colonies exceeds the number of colonies in the solvent controls by at least double, and a relationship between dose and response can be observed. Figure 3 shows dose-response curves of CNET phosphate and CNET-formaldehyde for TA100, TA1535, WP2*uvr*A, TA98 and TA1537 with and without S9mix. To give a concise presentation of results, specific activities (revertants/mg) were summarized for both compounds and compared with those of DNPH , DNPH-formaldehyde and positive controls in Table 1. The CNET phosphate showed significant mutagenic activities in TA100, TA1535 and WP2*uvr*A with (+S9) and without an external metabolic activation system (−S9) and negative in TA98 and TA1537. Meanwhile, DNPH showed greater specific activities in all strains than those of CNET. While CNET-formaldehyde was negative, DNPH-formaldehyde was positive in all strains. These *in vitro* testing results lead a conclusion than the use of CNET is preferable for safety handlings because of its weak mutagenicity rather than that of DNPH.

HPLC Analysis

HPLC analysis of the CNET coated silica gel yields the number of derivatives corresponds to the number of aldehydes and ketones collected on the adsorbent. In the HPLC chromatogram (Fig. 4), peaks of the CNET residue and CNET derivatives were well separated, and CNET-acetaldehyde gave two peaks corresponding to its two possible isomers, *E* and *Z*. Absorption spectra of acetaldehyde isomers showed similar curves with a maximum wavelength at 237 nm. But ratios between the two peak areas were not constant in the standard solution and eluted solutions of passive sampler. Then,

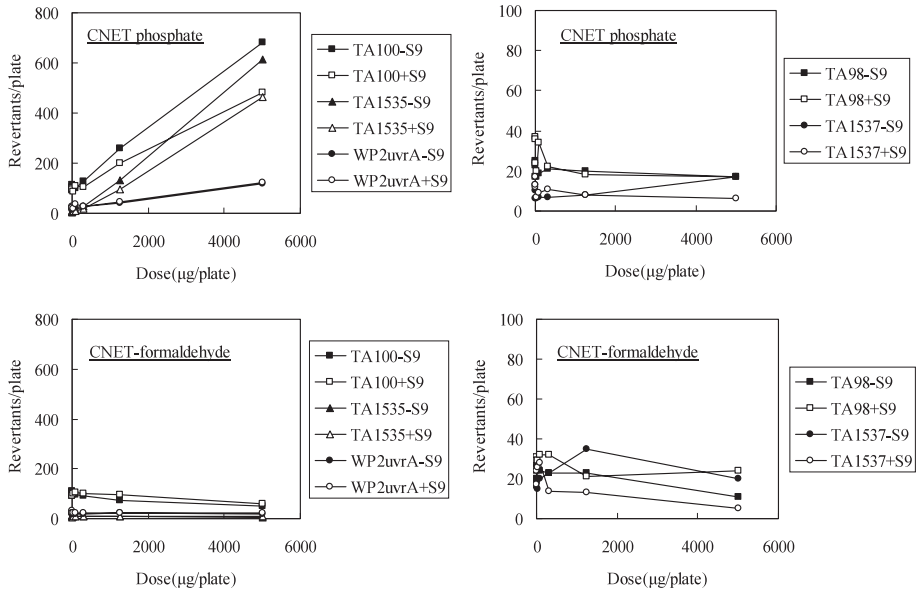
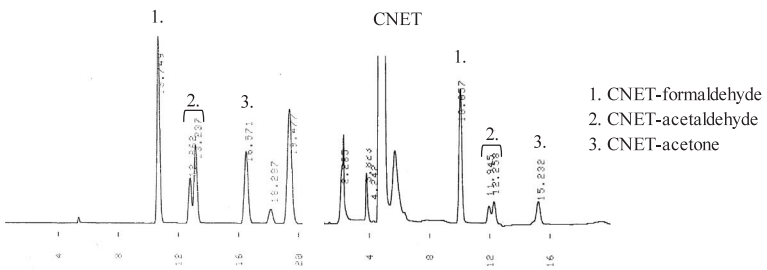


Fig. 3. Dose-response Curves of CNET Phosphate and CNET-formaldehyde for TA100, TA1535, WP2*uvr*A, TA98 and TA1537 with and without S9mix.

Table 1. Mutagenic Activity of CNET and Related Chemicals (revertants/mg)

Test substances	Base pair-substitution type						Frame-shift type			
	TA100		TA1535		WP2uvrA		TA98		TA1537	
	−S9	+S9	−S9	+S9	−S9	+S9	−S9	+S9	−S9	+S9
CNET phosphate	124	82	121	92	22	19	n	n	n	n
DNPH	2630	4560	188	359	241	256	5330	6560	461	564
CNET-formaldehyde	n	n	n	n	n	n	n	n	n	n
DNPH-formaldehyde	7080	9180	192	192	294	205	18000	2970	1590	576
Positive control	$4\times10^{7a)}$	$6\times10^{8b)}$	$6\times10^{5c)}$	$6\times10^{5d)}$	$1.6\times10^{7a)}$	$6\times10^{5e)}$	$2\times10^{6f)}$	$5\times10^{5g)}$	$9\times10^{3h)}$	$8\times10^{4d)}$

"n" denotes negative in mutagenic activity. Positive controls (μg/plate): *a*) 2-(2-furyl)-3-(5-nitro-2-furyl)acrylamide (0.01), *b*) 2-aminoanthracene (1), *c*) sodium azide (0.5), *d*) 2-aminoanthracene (2), *e*) 2-aminoanthracene (10), *f*) 2-(2-furyl)-3-(5-nitro-2-furyl)acrylamide (0.1), *g*) 2-aminoanthracene (0.5), *h*) 9-aminoacridine (80).



(a) Standard (10 μg/ml) (b) Indoor air sample

Fig. 4. Typical HPLC Chromatograms of the CNET Derivatives

we added up the two peaks of CNET-acetaldehyde for calibration and determination. Relative standard deviations (RSD) for repeated injection (n = 4) of 10 μg/ml of standard solutions were 4% in peak areas and 0.2% in retention times for each CNET derivative.

Determination of Sampling Rates

Sampling rates of the CNET-P were determined by establishing a relationship between collected amount of analyte by the passive sampler and air concentrations based on the results of small chamber experiments. Air concentration levels were set

considering Japanese guidelines for indoor air quality (0.1 mg/m^3 for formaldehyde and 0.048 mg/m^3 for acetaldehyde) and typical indoor air concentrations of chemicals in Japanese residences. Commonly, the sampling rate is expressed in terms of ml/min and derived from Eq.(3).

$$S\,(\mathrm{ml/min}) = \frac{W\,(\mu\mathrm{g})}{C\,(\mu\mathrm{g/ml})\;t\,(\mathrm{min})} \qquad (3)$$

Figure 5 shows relationship between air concentrations, C (mg/m^3) measured by the active sampling method and collected amounts of formaldehyde, acetaldehyde and acetone per hour, W/t (μg/h) by the passive sampler. Although exposure tests were conducted with varying sampling and environmental parameters (air concentration ranges, sampling duration: 8 and 24 hr, temperature: 10, 25 and 40°C and relative humidity (R.H.): 31–94%), the collected amounts of carbonyl compounds by the passive sampler showed good linearity to air concentrations in the chamber.

In the case where an adsorbent does not have enough trapping rate and capacity for analyte during the sampling, concentration of the given analyte at the end of diffusion layer is not zero and W/t will decrease with the time of sampling.[3)] Hence the sampling rate will also decrease with the time of exposure. However, significant differences were not found in the sampling rates for each carbonyl compound between 8 hr and 24 hr exposure tests. This means the CNET coated silica gel works as an effective trapping media for formaldehyde, acetaldehyde and acetone within 24 hr.

The air concentration of the sampled analyte can also have an effect on W/t and hence on S, when deposition flux of analyte on the trapping media depends on adsorption isotherm of analyte and adsorbent.[3, 18, 19)] However, this effect is negligible in this case, because W/t did not decrease with air concentrations within ranges given here.

The sampling rate of a passive sampler potentially depends on temperature: diffusion coefficient usually increases to the absolute temperature raised to the 1.66–1.83 power, air concentration varies inversely with absolute temperature according to the ideal gas law, increase in temperature decreases physical adsorption efficiency of the gas molecule, and heterogeneous reaction rate increases exponentially with absolute temperature obeying an Arrhenius law, if the gas molecule is firstly trapped on the surface of silica gel and then fixed as CNET derivatives. Then, temperature dependence was practically investigated at 15, 25 and 40°C, which seems to be realized in a workplace atmosphere and living environment. The results showed that effect of temperature was not apparent on the sampling rates under given conditions.

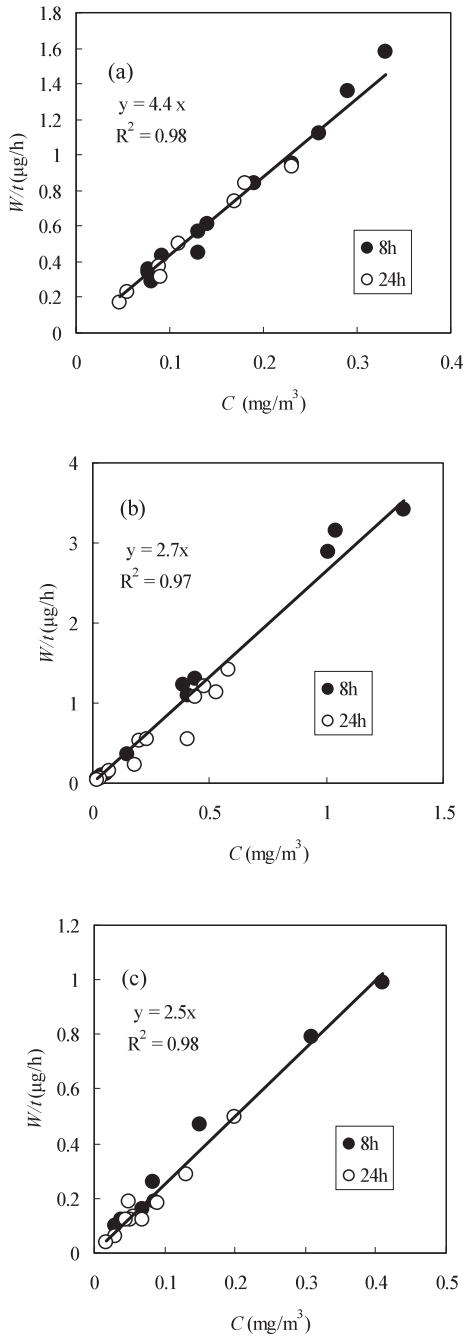


Fig. 5. Relationships between Air Concentrations, C in the Small Chamber and Collection Amounts of Carbonyl Compounds Per Hour by the Passive Sampler, W/t (Temperature: 10, 25 and 40°C, R.H.: 31–94%, Sampling Duration: 8 and 24 hr)
(a): formaldehyde, (b): acetaldehyde, (c): acetone.

Then, sampling rates of the CNET-P were derived from slopes of linear regression analy-

Table 2. Derived Sampling Rates S (ml/min) of CNET-P for Each Carbonyl Compound

formaldehyde	$n^{a)}$	acetaldehyde	n	acetone	n
74 ± 1.3	20	44 ± 1.3	20	42 ± 1.0	18

a) Number of pairs used for linear regression analysis.

sis for each carbonyl compound using both plots of 8 hr and 24 hr shown in Fig. 5 and summarized in Table 2. Sampling rate for formaldehyde was slightly smaller than those of previous passive samplers employing DNPH: DSD-DNPH (Sigma-Aldrich Japan, Supelco, 89 ml/min[12]) and Radiello® sampler (Fondazione Salvatore Maugeri IRCCS, Padova, Italy, 99 ml/min[22]), or greater than that of GMD badge (GMD Systems, Exton, PA, USA, 25 ml/min[9]). The sampling rates were high enough to realize short-term samplings in indoor environments such as workplace, museum, school, residences and so on.

Validation of Sampling Rates

The derived sampling rates of the CNET-P were validated in field tests. Figure 6 illustrates good agreement of the passive sampler responses with those of the active method for the determination of the three compounds using the sampling rates derived from the chamber experiment. The results show good linearity of the technique and suggest that reasonable accuracy can be expected after establishing the sampling rate under given exposure conditions.

The precision of the passive sampling method was assessed by field quartet measurements conducted in the university laboratory with 8 hr exposure. RSDs were 0.21% for 0.016 mg/m^3 of formaldehyde, 2.5% for 0.0089 mg/m^3 of acetaldehyde and 0.69% for 0.063 mg/m^3 of acetone.

Effect of Face Velocity on the Sampling Performance

Effect of face velocity on the sampling rate of the passive sampler potentially depends on the performance of draft shielding of a diffuser. Then, collection amounts of carbonyl compounds were investigated by varying a face velocity from 0 to 4 m/s in the laboratory air (temperature: 25°C, R.H.: 30–50%). The results showed the collection amounts of carbonyl compounds, W (μg) slightly increased with face velocity, v (ml/min), as follows.

$$W_{formaldehyde} = 0.015v + 0.088 \ (R^2 = 0.86, n = 6)$$
$$W_{acetaldehyde} = 0.0024v + 0.038 \ (R^2 = 0.93, n = 6)$$

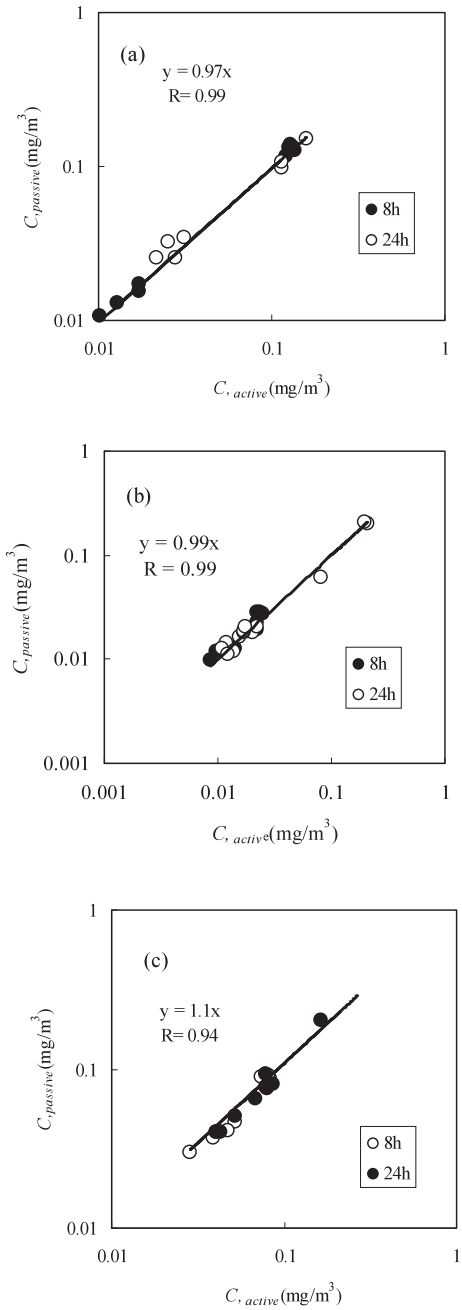


Fig. 6. Comparison of Indoor Air Concentrations of Carbonyl Compounds Measured by the Passive Sampler with Those by the Active Sampling Method (Field Measurements, Temperature: 22–30°C, R.H.: 53–75%, Sampling Duration: 8 and 24 hr)
(a): formaldehyde, (b): acetaldehyde, (c): acetone.

$$W_{acetone} = 0.033v + 0.78 \ (R^2 = 0.85, n = 6)$$

RSDs were 16% for formaldehyde, 8.6% for acetaldehyde and 6.2% for acetone with face velocity from 0 to 4 m/s. This means face velocity showed a little influence on the sampling performance of CNET-P when using it in indoor environment.

Influence of Ozone

Potential influence of ozone on the CNET was investigated by bubbling 0.8 ppm of ozone to 0.01 mg/ml of CNET or DNPH/acetonitrile solution. While 90% of DNPH was lost by bubbling ozone for 5 min, loss of CNET was only 9%. This means CNET is much more robust to ozone than DNPH. Only one product was formed when CNET reacted with ozone. The product, which has maximum absorption wavelength at 260 nm, has not been identified yet. However, the retention time of the unknown product is 7.5 min and tailing of the peak does not interfere with other peaks (*cf.* retention time of CNET-formaldehyde is 10 min as shown in Fig. 4). On the other hand, reaction products with formaldehyde were relatively unstable to ozone, probably due to addition of ozone to C=N double bond in the products. However, while loss of DNPH-formaldehyde was found to be >99% by bubbling ozone for 5 min, that of CNET-formaldehyde was 30%. Fragment peaks, produced by the reaction CNET-formaldehyde and ozone, were very small and eluted within 6.5 min. This shows carbonyl compounds can be collected and determined with reduced interference of ozone when using CNET as collection media compared with DNPH.

Then, the passive samplers were exposed to mixed vapours of carbonyl compounds under ozone free, 0.1 ppm and 0.8 ppm of ozone atmospheres. Figure 7 shows collection amounts of carbonyl compounds collected by CNET-P and DSD-DNPH in the small chamber. As can be seen, the collection amounts of carbonyls by DNPH-based sampler were apparently decreased under elevated ozone concentrations. On the contrary, no significant difference was found in the samples collected by CNET-P even at 0.8 ppm of ozone atmospheres. This is especially advantageous for CNET-based passive sampler when carbonyl compounds have to be determined in matrices that also contain ozone.

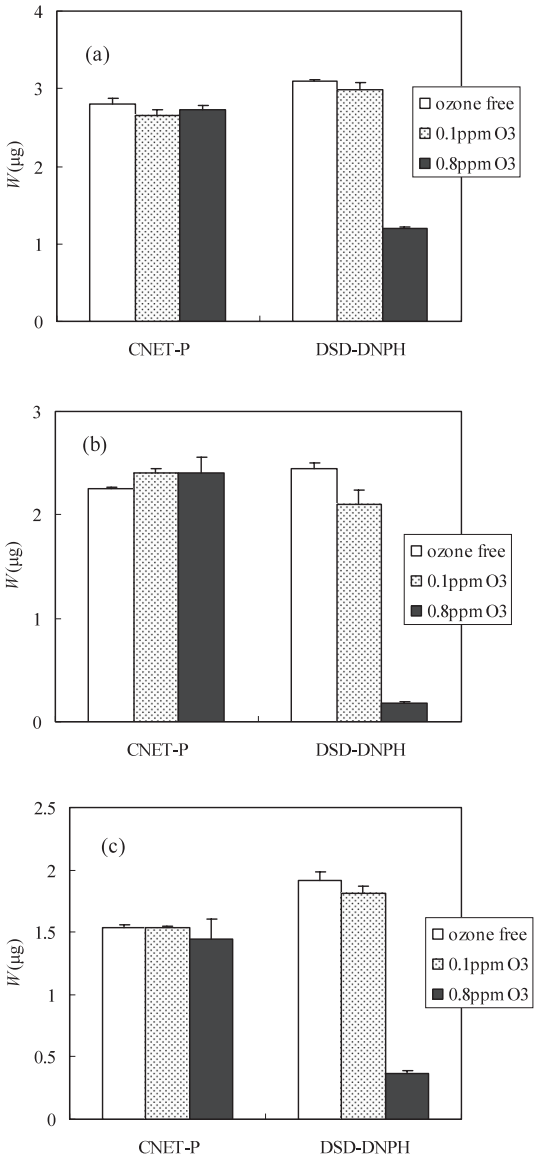


Fig. 7. Collection Amounts of Carbonyl Compounds under Ozone-free, 0.1 ppm and 0.8 ppm of Ozone Atmospheres by CNET-P and DSD-DNPH (Chamber Experiment, Temperature: 25°C, R.H.: 50%, Sampling Duration: 8 hr, Bar Shows Standard Deviations of Triplicate Measurements)
(a): formaldehyde, (b): acetaldehyde, (c): acetone.

Table 3. LOD and LOQ for the Determination of Carbonyl Compounds by CNET-P, Calculated Based on the Blank Samplers Stored in a Laboratory Refrigerator for 6 Months

Substance	n	m_B *a)* (μg)	S.D.	LOD (mg/m^3)		LOQ (mg/m^3)	
				8 hr	24 hr	8 hr	24 hr
formaldehyde	10	0.027	0.012	0.0010	0.00033	0.0033	0.0011
acetaldehyde	10	0.042	0.011	0.0015	0.00051	0.0051	0.0017
acetone	10	0.081	0.018	0.0026	0.00088	0.0088	0.0029

a) m_B denotes an average of storage blanks.

Blank Level, Limit of Detection (LOD) and Limit of Quantitation (LOQ)

Blank levels of the prepared passive sampler before storage were very low with an average loadings of 7.3 ng formaldehyde/sampler [standard deviation (S.D.) = 0.87, $n = 3$], 8.6 ng acetaldehyde/sampler (S.D. = 1.9, $n = 3$) and 55 ng acetone/sampler (S.D. = 2.4, $n = 3$). However, slight increase was found in storage blanks, which were stored for 6 months in sealed bags made of laminated aluminium in our laboratory refrigerator: 27 ng formaldehyde/sampler (S.D. = 12, $n = 10$), 42 ng acetaldehyde/sampler (S.D. = 11, $n = 10$) and 81 ng acetone/sampler (S.D. = 18, $n = 10$) as shown in Table 3. In this case, LOD of the sampler was calculated as triple the standard deviation of the storage blanks. Similarly, LOQ was calculated as ten-fold the standard deviation of the storage blanks. The LOD and LOQ were obtained for 8 hr- and 24 hr-sampling duration following the analytical procedure described above and summarized in Table 3. The results show the CNET-P is applicable for the determination of analytes at $\mu g/m^3$ level. As a reference, DSD-DNPH, which prevails in Japan as a passive sampler for carbonyl compounds, was obtained from commercial source. Its blank level was found relatively higher than those of CNET-P with an average loadings of 38 ng formaldehyde/sampler (S.D. = 2.7, $n = 3$), 88 ng acetaldehyde/sampler (S.D. = 1.3, $n = 3$) and 91 ng acetone/sampler (S.D. = 7.0, $n = 3$). Thus, the lower blank levels of carbonyl compounds in CNET-P are advantageous in the analytical sensitivity.

In conclusion, CNET has been developed as a new reactive trapping reagent for carbonyl compounds in air. In this study, we investigated the CNET as a potential alternative to DNPH as trapping reagent in the passive sampling device and lead the following evidences. The use of CNET is preferable in safety handlings because of its lower mutagenic activities than those of DNPH. Carbonyl compounds can be collected and determined with reduced interference of ozone when using CNET, because the CNET is less degradable by exposure to ozone than DNPH. The passive sampler, CNET-P was practically used for determination of formaldehyde, acetaldehyde and acetone in indoor air and gave similar results to active samplings with DNPH cartridges, using sampling rates determined by small chamber experiments. Lower blank levels of carbonyl compounds in CNET-P enable to determine analytes at $\mu g/m^3$ level. Therefore, the CNET is a possible alternative to DNPH in the passive sampler for the determination of formaldehyde, acetaldehyde and acetone in indoor air.

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